Technetium Diazenido-complexes. Part 2.[1] Substitution Chemistry of [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] and the Synthesis of Technetium Diazenido-complexes Directly from [NH$_4$][TcO$_4$]†

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The bis(diazenido)technetium(III) complex [TcCl(NNR)$_2$(PPh$_3$)$_2$] (R = C$_6$H$_4$Cl-4) reacted with bidentate ligands L with loss of one diazenide ligand to give [Tc(NNR)L$_2$(PPh$_3$)] (L = S$_2$CNR$_2$) and [TcCl(NNR)L(PPh$_3$)$_2$] (HL = maltol) in high yield. With dianionic tetradentate ligands L' complexes of the type *cis*-[Tc(NNR)L'(PPh$_3$)] [L' = dianion of *N,N'*-bis(salicylidene)ethane-1,2-diamine (salen), S(CH$_2$)$_2$NMe(CH$_2$)$_2$NMe(CH$_2$)$_2$S or O$_2$S(CH$_2$)$_2$NMe(CH$_2$)$_2$NMe(CH$_2$)$_2$SO$_2$] were obtained. The crystal structure of the complex with L' = salen has been determined. It shows pseudo-octahedral co-ordination about the Tc with the NNR and PPh$_3$ ligands *cis*. Direct reaction of [TcO$_4$]$^-$ with arylhydrazine hydrochlorides generated a diazenide species *in situ* which reacts with S$_2$CNR$_2$ to give [TcCl(NNR)$_2$(S$_2$CNR$_2$)$_2$] and 2,2'-bipyridine (bipy) to give [TcCl(NNR)(bipy)$_2$]$^+$ isolated as a BPh$_4^-$ salt.

Much of the current interest in the co-ordination chemistry of technetium relates to the possible application of its complexes in medical imaging. Many of the complexes currently in clinical use involve a polydentate ligand arrayed around a technetium(V) oxo or dioxo core, and we have been involved in the development of new cores involving species with metal–nitrogen multiple bonds. There is at the moment considerable emphasis on the construction of technetium non-essential imaging agents where the targetting ability of the complex resides in a biologically active molecule conjugated with it. This is usually achieved by covalent bonding of the biologically active component to a polydentate ligand, which can present considerable organic synthesis problems when it comes to fine tuning the biodistribution of the conjugate. We have as a long-term objective the linking of the bioactive molecule to a core involving diazenide, hydrazide or imide ligands *via* the nitrogen substituents. In earlier publications we reported preliminary details of the synthesis of diazenide, hydrazide and imide complexes[2] and the complete characterisation of a series of tertiary phosphine diazenido-complexes.[1] Here we describe the substitution chemistry of the tertiary phosphine complexes with bi- and tetra-dentate ligands and the synthesis of the diazenide core in one step directly from pertechnetate. This last step is significant in the context of radiopharmaceutical development as all imaging kits use [^{99m}TcO$_4$]$^-$ as the starting material.

Results and Discussion

Substitution Chemistry of [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$].—The analytical and spectroscopic data for the complexes prepared in this work are given in Table 1. The bidentate sulfur-donor Na[S$_2$CNMe$_2$] reacted with [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] in boiling absolute alcohol to give the novel orange crystalline technetium(III) complex *cis*[Tc(NNC$_6$H$_4$Cl-4)(S$_2$CNMe$_2$)$_2$(PPh$_3$)] **1** in good yield. The 4-Cl derivative was used since the simple phenyldiazenide analogue is believed to have a polymeric structure, and is inert to substitution.[1] Complex **1** is quite air-stable both in solution and the solid state. X-Ray-quality crystals were obtained from CH$_2$Cl$_2$–Et$_2$O. The crystal structure of **1** has been determined and reported previously.[3] The structural details of this, the first fully structurally characterised technetium dithiocarbamato-diazenido-complex, will not be discussed at length here except for comparison with the structure reported in this work.

The elemental analysis and spectroscopic data for complex **1** confirm its formulation. Repeated recrystallisation failed to give better elemental analysis data. From the analytical data and the crystallographic analysis it is apparent that **1** occludes variable amounts of CH$_2$Cl$_2$ in the crystal lattice.[3] The room-temperature ^{1}H NMR spectrum exhibits four sharp singlets assigned to the four non-equivalent methyl groups of the two dithiocarbamate ligands. This spectrum is consistent with a *cis* co-ordination geometry and restricted rotation about the C–N bonds of the dithiocarbamate ligands as confirmed by the X-ray structural analysis.[3] A *trans* co-ordination geometry with unrestricted rotation about the dithiocarbamate C–N bonds would give a spectrum exhibiting a single resonance for the equivalent methyl groups. No ^{31}P NMR resonance attributable to the singly co-ordinated triphenylphosphine ligand was observed at room temperature, but this is not uncommon for technetium phosphine complexes owing to the quadrupole moment of the ^{99}Tc nucleus. The reactions of [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] with other sodium dithiocarbamates such as Na[S$_2$CNEt$_2$] and Na[S$_2$CNMe(Ph)] were also attempted and gave solutions which possessed single Tc-containing species on HPLC analysis [tetrahydrofuran (thf), β^- detection]. However, the high solubility prevented successful isolation of pure crystalline solids.

Reaction of [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] with an excess of maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one, Hhmpo) in absolute ethanol under reflux gives dark orange crystalline

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and spectroscopic data for complexes prepared

Complex	HPLC[a] retention time/min	Analysis (%) [Found (calc.)]				Infrared[b] (cm^{-1})	^{1}H NMR[c] (δ)
		C	H	N	Cl		
1 $[Tc(NNC_6H_4Cl\text{-}4)(S_2CNMe_2)_2(PPh_3)]$[d]	13.6, single species	48.0 (48.5)	4.0 (4.2)	6.8 (7.6)	4.6 (4.8)	1615, 1570 (NN) 1525 (CN)	2.92 (3 H, s, CH_3) 3.06 (3 H, s, CH_3) 3.31 (3H, s, CH_3) 3.39 (3 H, s, CH_3) 5.27 (CH_2Cl_2) 6.8–7.7 (19 H, m, Ph)
2 $[TcCl(NNC_6H_4Cl\text{-}4)(hmpo)(PPh_3)_2]$[e]	10.0, single species	59.7 (62.4)	4.1 (4.2)	3.0 (3.0)	7.7 (7.7)	1615, 1560 (NN)	2.21 (3 H, s, CH_3) 5.63 [1 H, d, $^3J_{HH}$ = 4 Hz, C=CH] 6.92 [1 H, d, $^3J_{HH}$ = 4 Hz, C=CH] 7.0–8.0 (34 H, m, Ph)
3 $[Tc(NNC_6H_4Cl\text{-}4)(salen)(PPh_3)]$	11.6, single species	61.8 (62.6)	4.4 (4.3)	7.2 (7.3)	4.8 (4.6)	1600, 1610, 1620 (NN) 1540 (CN)	4.0 (4 H, br m, CH_2CH_2) 6.0–7.6 (22 H, m, Ph) 8.14 (2 H, s, N=CH)
4 $[Tc(NNC_6H_4Cl\text{-}4)\{O_2S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2SO_2\}(PPh_3)]$						1530, 1595 (NN) 1020, 1125 (S=O)	
5 $[TcCl(NNC_6H_4Cl\text{-}4)_2(S_2CNMe_2)_2]$	16, 12 (3:1)	33.3 (33.1)	3.2 (3.1)	12.3 (12.8)	15.9 (16.3)	1565, 1590 (NN) 1525 (CN)	3.18 (6 H, s, CH_3) 3.56 (6 H, s, CH_3) 3.32 (6 H, s, CH_3) 6.84 (12 H, d, aryl H) 7.16 (12 H, d, aryl H) 7.48 (4 H, d, aryl H) 7.81 (4 H, d, aryl H)
6 $[Tc(NNC_6H_4Cl\text{-}4)_2(hmpo)_2]Cl$	12.0	43.1 (43.4)	2.5 (2.7)	7.9 (8.4)	16.3 (16.0)	1545, 1560 (NN) 1606 (C=C) 1660 (C=O)	2.34 (s, CH_3) 6.93 (d, CH) 7.69 (d, CH)
7 $[TcCl(NNC_6H_4Cl\text{-}4)(bipy)_2][BPh_4]$	10.2	65.8 (66.3)	4.2 (4.4)	8.8 (9.3)	8.1 (7.8)	1575 (NN) 1605, 1625 (C=C)	7.10 (d, diazenide) 8.97 (d, bipy) 9.42 (d, bipy)
8 $[TcCl_2(NNC_6H_4Cl\text{-}4)L^1(NH_3)]$	14.0	29.1 (30.0)	4.2 (3.8)	12.3 (12.5)	18.4 (19.0)	3040, 3140 (NH) 1650, 1710 (C=O) 1570, 1590 (NN)	2.48 (s, CH_2) 3.35 (s, CH_3) 6.55 (d, aryl H) 6.98 (d, aryl H) 7.12 (s, NH_3)
9 $[TcCl(NNC_6H_4Cl\text{-}4)L^2][BPh_4]$	11.2	57.8 (57.1)	6.0 (5.3)	7.1 (7.0)	9.0 (8.9)	1530, 1565, 1600 (NN)	2.49 (d, CH_2) 3.03 (br s, CH_3) 3.41 (br s, CH_3) 6.75–7.44 (m, Ph)
10 '$[TcCl(NNC_6H_4Cl\text{-}4)(HL^3)]$'	10.4	44.0	7.7	15.6	12.6		

[a] Measurements were made in thf–aqueous $[NBu_4][BF_4]$ using a Gilson model 702 isocratic HPLC system fitted with a poly(styrene–divinylbenzene) copolymer column, HM Holochrome UV detection module (set at 250 nm) and custom-built (Amersham International) β^- detection system. [b] Nujol mull, KBr plates. [c] In $CDCl_3$ solution. [d] Crystallises as the $0.25CH_2Cl_2$ solvate. [e] $\delta(^{31}P)$ 30.0(s).

$[TcCl(NNC_6H_4Cl\text{-}4)(hmpo)(PPh_3)_2]$ **2**. This novel 18-electron (assuming the diazenide ligand is singly bent) diazenido-complex is one of the few reported technetium complexes containing the maltol ligand and is formally analogous to $[ReCl(NNCOPh)(hmpo)(PPh_3)]$.[4] X-Ray crystallographic analysis of crystals of **2** recrystallised from CH_2Cl_2–Et_2O was not successful due to slow loss of solvent from the crystals. The analytical and spectroscopic data are, however, consistent with the formulation proposed. The attempted substitution of $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ with the bidentate oxygen-donor ligands catechol and 2-hydroxy-1,4-naphthoquinone in boiling alcohol gave reaction mixtures which resisted numerous attempts to prepare pure solids.

The tetradentate ONNO(2−) ligand H_2salen [*N,N′*-bis(salicylidene)ethane-1,2-diamine] reacts with $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ in boiling methanol–toluene in the presence of NEt_3 to give the neutral dark green technetium(III) diazenido-complex *cis*-$[Tc(NNC_6H_4Cl\text{-}4)(salen)(PPh_3)]$ **3** in good yield. The *cis* co-ordination geometry has been confirmed by X-ray structural analysis (see below). Reaction of $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ with the obligately planar ONNO(2−) ligand H_2salphen [*N,N′*-bis(salicylidene)-*o*-phenylenediamine] gave only unreacted starting materials. This suggests that a *cis* co-ordination geometry of the N_2R and PPh_3 ligands may be preferred.

The flexible tetradentate $N_2S_2(2-)$ ligands *N,N′*-bis(2-mercaptoethyl)-*N,N′*-dimethylethane-1,2-diamine, H_2L^1 and *N,N′*-bis(2-mercaptopropionyl)ethane-1,2-diamine H_2L^2 were synthesised by literature methods[5,6] and treated with the bis(diazenido) starting material $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_{32}]$ in boiling alcohol in the presence of NEt_3 to give an orange crystalline material and an insoluble dark brown solid, respectively. The product with H_2L^2 was too insoluble for satisfactory spectroscopic analysis. Elemental analysis performed on the dried product isolated directly from the reaction mixture did not give reproducible results and the formulation of a mono(diazenido)-N_2S_2 co-ordinated polymeric species is suggested.

The orange crystalline material obtained from reaction of $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ and H_2L^1 is formulated as a TcNNR complex of the bis(sulfinato) derivative of the N_2S_2 ligand, obtained by facile aerial oxidation of the co-ordinated thiol sulfur donors of ligand H_2L^1, $[Tc(NNC_6H_4Cl\text{-}4)\{O_2S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2SO_2\}(PPh_3)]$ **4** as shown in Scheme 1. This facile aerial ligand oxidation is directly analogous to that which occurs for the rhenium derivative (Scheme 2).[7] The elemental and spectroscopic analysis confirms the formulation of **4**. The infrared spectrum exhibits medium-to-intense stretching frequencies at 1020 and 1125 cm^{-1} assigned to ν(NN) and at 1020 and 1195 cm^{-1} assigned to $\nu_{sym}(SO_2)$ and $\nu_{asym}(SO_2)$ respectively.

The chemistry of the Re–NNR complexes of such N_2S_2 ligands appears to be dramatically influenced by the R group of the organodiazenide. When R = COPh or CO_2Me the $[Re(NNR)(L^1)(PPh_3)]$ complexes are stable towards oxidation, whereas when R = C_6H_4X-4 (X = halogen) the complexes undergo facile aerial oxidation to the bis(sulfinato) species $[Re(NNR)\{O_2S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2SO_2\}(PPh_3)]$.[7]

$$[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2] \xrightarrow{(i)} [Tc(NNC_6H_4Cl\text{-}4)L^1(PPh_3)_2] \xrightarrow{(ii)} [Tc(NNC_6H_4Cl\text{-}4)\{O_2S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2SO_2\}(PPh_3)]$$

Scheme 1 (*i*) L^1; (*ii*) air oxidation

$$[Re(NNC_6H_4Cl\text{-}4)L^1(PPh_3)] \xrightarrow{(i)} [Re(NNC_6H_4Cl\text{-}4)\{O_2S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2SO_2\}(PPh_3)]$$

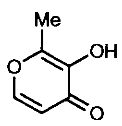
Scheme 2 (*i*) Air oxidation

Complex **4** represents the first technetium complex with a TcNNR core surrounded by a facultative tetradentate ligand possessing an N_2S_2 donor set ligated through the nitrogen and sulfur atoms.

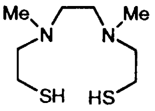
Reaction of the bis(diazenido) starting material $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ with the tetradentate amine oxime ligands H_4L^3 and H_4L^4 under a variety of quite forcing conditions resulted only in recovery of unreacted starting materials.

Molecular Structure of cis-$[Tc(NNC_6H_4Cl\text{-}4)(salen)(PPh_3)]$ **3**.—An ORTEP[8] representation of the structure of *cis*-$[Tc(NNC_6H_4Cl\text{-}4)(salen)(PPh_3)]$ **3** is shown in Fig. 1 along with the associated atom numbering scheme. Selected bond lengths and angles are given in Table 2.

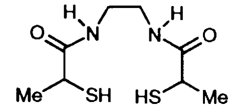
Complex **3** has distorted octahedral co-ordination with *cis*-N_2R and PPh_3 ligands, consistent with the spectroscopic analysis. The tetradentate salen ligand deviates significantly from planar geometry. The diazenide ligand adopts the singly



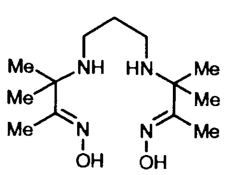
Maltol
(Hhmpo)



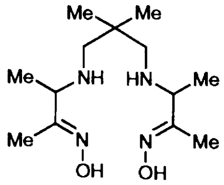
H_2L^1



H_2L^2



H_4L^3



H_4L^4

Table 2 Selected bond lengths (Å) and angles (°) for $[Tc(NNC_6H_4Cl\text{-}4)(salen)(PPh_3)]$

Tc–P	2.414(3)	C(1)–N(1)	1.285(14)
Tc–O(1)	2.087(6)	C(2)–N(2)	1.258(13)
Tc–O(2)	2.064(6)	C(3)–N(1)	1.462(14)
Tc–N(1)	2.057(8)	C(4)–N(2)	1.477(13)
Tc–N(2)	2.101(9)	C(4)–C(3)	1.524(13)
Tc–N(3)	1.764(8)	C(12)–O(1)	1.307(12)
N(3)–N(4)	1.241(11)	C(26)–O(2)	1.320(11)
N(4)–C(31)	1.421(13)		
P–Tc–O(1)	92.0(2)	N(2)–Tc–N(3)	89.4(3)
P–Tc–O(2)	93.5(2)	Tc–O(1)–C(12)	124.0(5)
P–Tc–N(1)	98.7(2)	Tc–O(2)–C(26)	124.6(6)
P–Tc–N(2)	175.6(2)	Tc–N(1)–C(1)	128.1(7)
P–Tc–N(3)	89.3(2)	Tc–N(1)–C(3)	109.7(6)
O(1)–Tc–O(2)	84.1(2)	C(1)–N(1)–C(3)	117.5(8)
O(1)–Tc–N(2)	89.0(3)	Tc–N(2)–C(2)	125.9(2)
O(1)–Tc–N(3)	176.0(3)	Tc–N(2)–C(4)	114.9(6)
O(2)–Tc–N(1)	161.6(3)	C(2)–N(2)–C(4)	119.1(9)
O(2)–Tc–N(2)	90.8(3)	Tc–N(3)–N(4)	173.6(7)
O(2)–Tc–N(3)	99.6(3)	N(3)–N(4)–C(31)	119.4(7)
N(1)–Tc–N(2)	77.2(3)	N(1)–C(3)–C(4)	105.5(8)
N(1)–Tc–N(3)	94.3(3)	N(2)–C(4)–C(3)	107.5(8)

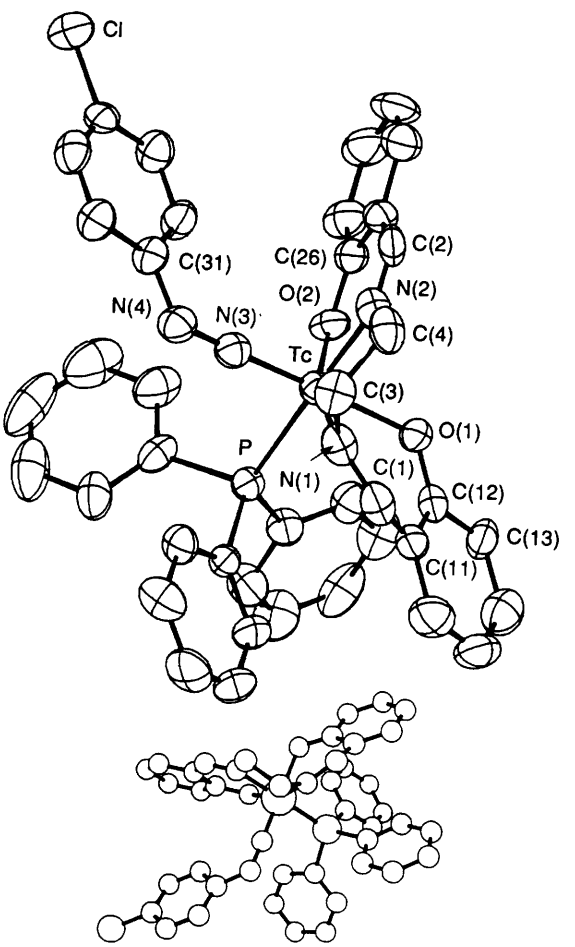


Fig. 1 An ORTEP representation of the molecular structure of complex **3**

bent geometry with a Tc–N(3)–N(4) bond angle of 173.6(7)° and a Tc–N(3) bond length of 1.764(8) Å which is very similar to that of the structurally characterised *cis*-$[TcCl(NNC_6H_4Cl\text{-}4)(S_2CNMe_2)_2(PPh_3)]$ **1** [Tc–N(3)–N(4) 178.6(4)°, Tc–N(3) 1.763(3) Å].[3] The N_2R ligand in **3** can therefore be regarded as a three-electron neutral or four-electron monoanionic donor giving the complex an overall 18-electron configuration. The Tc–P distance of 2.414(3) Å is closely similar to that of 2.422(2) Å in complex **1**.[3]

Preparation of Technetium Diazenido-complexes directly from $[NH_4][TcO_4]$.—The next phase of this work was to investigate whether a variety of non-phosphine ligands could be co-ordinated around the diazenidotechnetium core when generated *in situ* directly from ammonium pertechnetate and arylhydrazine hydrochloride.

Reaction of the orange alcoholic solution prepared from $[NH_4][TcO_4]$ and $RNHNH_2{\cdot}HCl$ with $Na[S_2CNMe_2]$ under reflux gave a neutral dark red-purple solid analysing as the novel technetium(v) complex $[TcCl(NNC_6H_4Cl\text{-}4)_2(S_2CNMe_2)_2]$ **5**. The ^1H NMR spectrum indicates the presence of two types of inequivalent dithiocarbamate ligands (ratio 2:1) and two aryldiazenide ligands and pentagonal-bipyramidal geometry is inferred. It also suggests the presence of two species in solution, one being six- and the other seven-co-ordinate, with the former predominating in a 3:1 ratio. The HPLC analysis (thf, β^- detection) also shows two ^{99}Tc-containing species in the ratio 3:1 (major species, retention time 16 min; minor, 12 min). The two different species present in solution may be due to ionisation of the chloro group (Scheme 3). However, although the isolated solid appears to be quite stable, unfortunately the postulated co-ordination geometry could not be confirmed by X-ray crystallography despite several attempts to obtain suitable crystals.

$$[TcCl(NNC_6H_4Cl\text{-}4)_2(S_2CNMe_2)_2] \longleftrightarrow [Tc(NNC_6H_4Cl\text{-}4)_2(S_2CNMe_2)_2]Cl$$

Scheme 3

Similar reaction with maltol gave solid purple $[Tc(NNC_6H_4Cl\text{-}4)_2(hmpo)_2]Cl$ **6**, which is formulated as being six-co-ordinate, consistent with the analytical and spectroscopic data.

Reaction of the orange solution with 2,2′-bipyridine (bipy) resulted in a brown cationic complex isolated as its BPh_4^- salt and formulated as the six-co-ordinate technetium(III) monodiazenido-complex $[TcCl(NNC_6H_4Cl\text{-}4)(bipy)_2][BPh_4]$ **7**. Complex **7** exhibited a very complex ^1H NMR spectrum indicating inequivalent bipy ligands and suggesting a *cis*-co-ordination geometry. This interesting result shows that the bipy ligand can co-ordinate around a $Tc^{III}(N_2R)$ core when the complex is generated *in situ*. It seems that the sterically bulky PPh_3 ligands in $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ prevent the substitution reaction in some way and the bis(diazenide) complex does not react with bipy. This is somewhat surprising since technetium(II) complexes of the general type *cis*-(X), *trans*-(P)-$[TcX_2(PR_2R')_2L]$, where X = Cl or Br, PR_2R' = PMe_2Ph or $PEtPh_2$ and L = bipy or phen (1,10-phenanthroline), have been synthesised by the replacement of one halide and one phosphine ligand of *mer*-$[TcX_3(PR_2R')_3]$ by the appropriate bidentate ligand in ethanol under reflux.[9,10]

Reaction of the orange solution of the diazenido-precursor with H_2salen gave a grey-green solid which lacked any evidence for co-ordinated salen. The product was tentatively assigned as a very hydrophilic complex species of the type $[TcX_n(N_2R)_n]$.

The N_2S_2 ligand H_2L^1 yielded a neutral dark green complex which eluted as a single species on HPLC analysis. Infrared and ^1H NMR spectra indicate the presence of a co-ordinated ammonia ligand. The presence of a co-ordinated N_2R group is also seen. The complex is formulated as the six-co-ordinate technetium(v) species, $[TcCl_2(NNC_6H_4Cl\text{-}4)L^1(NH_3)]$ **8** with the N_2S_2 ligand acting in a bidentate manner through both sulfur atoms. Other examples of N_2S_2 ligands behaving in a bidentate fashion *via* the two sulfur atoms are known.[11,12] The decomposition of multiply bonded nitrogen-containing ligands to form ammonia complexes of type $[ReX_2(NNR)(NH_3)(PR_3)_2]$ also occurs.[13,14] If the formulation of complex **8** is correct, then this would be a rare example of a technetium(v) diazenido-complex.

Similar reaction with H_2L^2 gave a khaki coloured cationic complex which eluted as a single species on HPLC analysis. This product is formulated as the octahedral technetium(v) complex *trans*-$[TcCl(NNC_6H_4Cl\text{-}4)L^2][BPh_4]$ **9**, with *trans*-Cl and -N_2R ligands and the tetradentate ligand spanning the equatorial plane. The analytical and spectroscopic data are consistent with this formulation. The contrasting ability of L^1 and L^2 to co-ordinate the diazenido-technetium core is expected due to the greater basicity and therefore greater donating ability of the nitrogen atoms of L^2.

Reaction of the orange diazenido-solution with H_4L^3 gave a neutral turquoise solid which contained co-ordinated L^3 (NMR) and eluted as a single Tc-containing species on HPLC analysis. The product is tentatively formulated as the chloromonodiazenido-complex **10**, which could contain Tc^V or Tc^{III} depending on the extent of deprotonation of the H_4L^3 ligand. However, reproducible analytical data could not be obtained.

Conclusion

We have demonstrated that a wide variety of ligand geometries can be accommodated around the $Tc(N_2R)$ core. These novel complexes may be prepared in high yields either by substitution of the useful bis(diazenido) starting material [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] with the appropriate coligand(s) or from 'one-pot' reactions involving [NH$_4$][TcO$_4$], arylhydrazine hydrochloride, and the appropriate coligand in alcoholic solution. The successful development of such *in situ* synthesis of diazenidotechnetium complexes is potentially interesting in the context of development of radiopharmaceuticals. An easy and direct synthesis to a stable, radiochemcially pure technetium complex is ideal for radiopharmaceutical kit formulations. The wide variety of different donor atom types that can be incorporated around the stable multiply bonded diazenidotechnetium core means that the ligands around the core may be easily and flexibly varied according to the specific biodistribution properties required.

The extrapolation of this TcNNR co-ordination chemistry to the γ-emitting ^{99m}Tc isotope and the resultant biodistribution studies will be reported elsewhere.

Experimental

Methods.—**CAUTION**: Technetium-99 is a low energy β^--particle emitter (292 keV, *ca.* 4.67×10^{-14} J; $t_{\frac{1}{2}} = 2.14 \times 10^5$ year). Normal radiation safety procedures were followed at all times. All manipulations of solutions and solids were performed in an efficient fumehood to prevent contamination and inadvertent inhalation. When handled in milligram quantities ^{99}Tc-containing compounds do not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremsstrahlung radiation is not a significant problem due to the low energy of the β^--particle emission. All preparations were performed under an atmosphere of purified dinitrogen using predried distilled solvents[15] unless otherwise stated. Solutions of 0.343 mmol dm^{-3} [NH$_4$][TcO$_4$] in 0.1 mol dm^{-3} aqueous ammonia were kindly supplied by Amersham International plc. All other reagents were obtained from Aldrich and used as received. The complex [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] was prepared as previously described.[1] Elemental analyses, IR, ^{1}H and ^{31}P NMR spectroscopy were carried out as described in ref. 1.

Preparation of Complexes by Substitution of [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$].—[Tc(NNC$_6$H$_4$Cl-4)(S$_2$CNMe$_2$)$_2$(PPh$_3$)] **1**. The complex [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] (0.139 g, 0.148 mmol) and Na[S$_2$CNMe$_2$] (0.08 g, 0.444 mmol) in absolute ethanol (2 cm^3) were heated under reflux for 1.5 h. After cooling, the orange precipitate was filtered off and dissolved in CH$_2$Cl$_2$ before passing down a Fluorisil™ column, eluting the orange band with CH$_2$Cl$_2$. The orange eluate was evaporated to dryness and the residue recrystallised from CH$_2$Cl$_2$–Et$_2$O to give dark orange crystals suitable for X-ray crystallography. Yield 0.072 g, 66%.

[TcCl(NNC$_6$H$_4$Cl-4)(hmpo)(PPh$_3$)$_2$] **2**. The complex [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] (0.145 g, 0.155 mmol) and maltol (0.059 g, 0.465 mmol) in absolute ethanol (2 cm^3) were heated under reflux for 2 h. After cooling to room temperature the orange precipitate was filtered off and recrystallised from CH$_2$Cl$_2$–Et$_2$O. Yield 0.03 g, 21%.

[Tc(NNC$_6$H$_4$Cl-4)(salen)(PPh$_3$)] **3**. The complex [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)] (0.100 g, 0.107 mmol), H$_2$salen (0.032 g, 0.119 mmol) and NEt$_3$ (0.40 cm^3, 0.239 mmol) in dry methanol–toluene (1 : 1, 3 cm^3) were heated under reflux for 2 h. After cooling, addition of diethyl ether gave a khaki-green solid, which was filtered off, washed with ether and dried. Yield 0.052 g, 63%. Recrystallisation from CH$_2$Cl$_2$–heptanes yielded very dark green crystals suitable for X-ray crystallographic analysis.

[Tc(NNC$_6$H$_4$Cl-4){O$_2$S(CH$_2$)$_2$NMe(CH$_2$)$_2$NMe(CH$_2$)$_2$SO$_2$}(PPh$_3$)] **4**. The complex [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] (0.108 g, 0.115 mmol), L^1 (0.026 g, 0.127 mmol) and NEt$_3$ (0.07 cm^3, 0.35 mmol) in dry methanol (2 cm^3) were heated under reflux for 1 h to give an orange mixture. After cooling, the orange product was filtered off, washed with ether and dried. Yield 0.046 g, 52%.

Preparation of Technetium Diazenido-complexes directly from [NH$_4$][TcO$_4$].—*General procedure.* Aqueous [NH$_4$][TcO$_4$] (0.5 cm^3, 0.181 mmol) was evaporated to dryness *in vacuo*. The compound 4-ClC$_6$H$_4$NHNH$_2$·HCl (0.142 g, 0.793 mmol) in dry methanol (2 cm^3) was added with stirring to give an immediate orange solution. After 10 min of stirring at room temperature, the appropriate coligand(s) were added.

[TcCl(NNC$_6$H$_4$Cl-4)$_2$(S$_2$CNMe$_2$)$_2$] **5**. Solid Na[S$_2$CNMe$_2$] (0.097 g, 0.543 mmol) was added to the orange solution and the resulting mixture was heated under reflux for 1.5 h. A dark red-purple mixture was obtained, from which a dark red-purple solid was collected by filtration after cooling and washed with methanol. Yield 0.086 g, 73%.

[Tc(NNC$_6$H$_4$Cl-4)$_2$(hmpo)$_2$]Cl **6**. Solid maltol (0.068 g, 0.543 mmol) was added to the orange solution which was heated under reflux for 1 h. The dark brown mixture was reduced to dryness *in vacuo* and the residue dissolved in CH$_2$Cl$_2$. This was layered with pentane and the solvents allowed to evaporate slowly. The dark purple solid obtained was filtered off and dried. Yield 0.090 g, 75%.

[TcCl(NNC$_6$H$_4$Cl-4)(bipy)$_2$][BPh$_4$] **7**. Solid bipy (0.085 g, 0.543 mmol) was added to the orange solution which was heated under reflux for 2 h. After cooling to room temperature, Na[BPh$_4$] (0.062 g, 0.181 mmol) was added to the dark brown solution and the mixture was stirred for 1 h. The brown solid was filtered off, washed with methanol and ether and dried. Yield 0.150 g, 92%.

[TcCl$_2$(NNC$_6$H$_4$Cl-4)L^1(NH$_3$)] **8**. The compound H$_2$L^1 (0.047 g, 0.199 mmol) was added to the orange solution and the mixture heated under reflux for 1.5 h. After cooling the dark green mixture, pentane (5 cm^3) was added and the mixture stirred for 1 h. A dark green solid was obtained upon filtration. Yield 0.093 g, 92%.

Table 3 Summary of crystal data, data collection and structure refinement for [TcCl(NNC$_6$H$_4$Cl-4)(salen)(PPh$_3$)]

Empirical formula	C$_{40}$H$_{33}$ClN$_4$O$_2$PTc
Colour, habit	Dark green prisms
M	766.15
Crystal system	Monoclinic
Space group	*P*2$_1$/*c*
a/Å	12.207(4)
b/Å	15.987(1)
c/Å	18.199(2)
β/°	100.16(4)
U/Å^3	3493.8
Z	4
D$_c$/g cm^{-3}	1.456
F(000)	1568
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo-Kα (λ = 0.710 73 Å)
T/K	297
Monochromator	Graphite
2θ range/°	2–48
Scan speed/° min^{-1}	3.3 (maximum)
Background measurement	90
Standard reflections	020, zero loss of intensity
Index ranges	*h* 0–14, *k* 0–18, *l* −20 to 20
Reflections collected	5978
Reflections observed	2623
Program used	Enraf-Nonius SDP v3.0[16]
Solution method	Patterson
Refinement method	Full-matrix least squares
Quantity minimised	$\Sigma w\Delta^2$
Hydrogen atoms	Determined from geometric criteria
Weighting scheme	$1/w = [\sigma(F^2) + (0.025F)^2 + 2.8]$
R (observed data)	0.052
R′	0.058

$[TcCl(NNC_6H_4Cl\text{-}4)L^2][BPh_4]$ **9**. The compound H_2L^2 (0.041 g, 0.199 mmol) was added to the orange solution and the mixture heated under reflux for 1.5 h. After cooling the dark brown solution, $Na[BPh_4]$ (0.062 g, 0.181 mmol) was added and the mixture stirred for 1 h. The khaki green solid was collected by filtration. Yield 0.095 g, 66%.

Complex **10**. The compound H_4L^3 (0.108 g, 0.398 mmol) was added to the orange mixture and heated under reflux for 1.5 h. A deep blue-green solution was obtained to which pentane (8 cm^3) was added and the mixture stirred for 1 h. A turquoise solid was obtained upon filtration. Yield 0.073 g, 74%.

X-Ray Crystallographic Analysis of Complex **3**.—The details of the crystal structure determination are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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